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Geochemistry of Metal-Organic Complexes In Naturally-Acidic Waters from Peatlands

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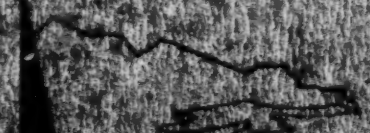
February 1986



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GEOCHEMISTRY OF METAL-ORGANIC COMPLEXES IN NATURALLY-ACIDIC WATERS FROM PEATLANDS

FINAL REPORT

submitted to

ENVIRONMENT CANADA

by

WILLIAM SHOTYK

February 1985

revised February 1986

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TABLE OF CONTENTS

PREFACE vii

SUMMARY ix

RÉSUMÉ xiii

ACKNOWLEDGEMENTS xvi

1.0 INTRODUCTION 1

2.0 OBJECTIVES 2

3.0 METHODS 3

- 3.1 Peat Chemistry
  - 3.1.1 Botanical composition, degree of decomposition and ash content of Luther Bog and Barrington Bog
  - 3.1.2 Inorganic chemistry of Luther Bog and Barrington Bog
    - 3.1.2.1 Al, Ca, Mg, Na, K, Fe and Mn by atomic absorption
    - 3.1.2.2 Cr, U, Zn, As and W by neutron activation
- 3.2 Peat pore water chemistry (Luther Bog)
  - 3.2.1 pH by glass combination electrode
  - 3.2.2 CO_2 and CH_4 by gas chromatography
  - 3.2.3 Al, Ca, Mg, Na, V, Cr, Mn and U by neutron activation
  - 3.2.4 Chloride, sulphate and oxalate by ion chromatography
- 3.3 Speciation calculations using GEOCHEM

4.0 RESULTS 8

- 4.1 Peat Chemistry
  - 4.1.1 Botanical composition, degree of decomposition and ash content of peats from Luther Bog and Barrington Bog
  - 4.1.2 Inorganic chemistry of Luther Bog and Barrington Bog peats
    - 4.1.2.1 Al, Ca, Mg, Na, K, Fe and Mn
    - 4.1.2.2 Cr, U, Zn, As and W

4.2 Peat pore water chemistry (Luther Bog)
4.2.1 pH
4.2.2 CO_2 and CH_4
4.2.3 Al, Ca, Mg, Na, V, Cr, Mn and U
4.2.4 Chloride, sulphate and oxalate
4.3 Speciation of metals in peatland waters

5.0 **DISCUSSION** 10
5.1 Physical chemistry of bog waters
5.1.1 pH
5.1.2 Redox chemistry
5.2 Chemical composition of surface waters and peat pore waters
5.2.1 Dissolved metals
5.2.2 Organic acids
5.3 Speciation of dissolved constituents in surface waters
5.3.1 pH
5.3.2 Redox chemistry
5.3.3 Dissolved metals
5.3.4 Organic ligands
5.3.5 Inorganic ligands

6.0 **CONCLUSIONS** 20
6.1 pH
6.2 Redox chemistry
6.3 Speciation of dissolved constituents

7.0 **RECOMMENDATIONS FOR FURTHER STUDY** 22
7.1 Physical chemistry of peatland waters
7.1.1 pH
7.1.2 Redox chemistry
7.2 Chemical composition of peatland waters
7.2.1 Dissolved metals
7.2.2 Inorganic ligands
7.2.3 Organic ligands
7.3 Speciation of dissolved constituents

8.0 **REFERENCES** 25

9.0 **FIGURES** 27

10.0 **TABLES** 31

LIST OF FIGURES

Figure 1. Location of Luther bog, Ontario.

Figure 2. Location of Barrington bog, Nova Scotia.

Figure 3. pH determination by direct insertion of glass combination electrode into wet peat and by filtering (0.22 um) pore water squeezed from the same samples.

LIST OF TABLES

Table 1. Operating conditions employed for Dionex model 20101 ion chromatograph.

Table 2. Botanical composition, degree of decomposition and ash content of peat samples from Luther Bog.

Table 3. Botanical composition, degree of decomposition and ash content of peat samples from Barrington Bog.

Table 4. Al, Ca, Mg, Na, K, Fe and Mn in Luther Bog peat samples by atomic absorption.

Table 5. Al, Ca, Mg, Na, K, Fe and Mn in Barrington Bog peat samples by atomic absorption.

Table 6. Cr, U, Zn, As and W in Luther Bog peat samples by neutron activation.

Table 7. Cr, U, Zn, As and W in Barrington Bog peat samples by neutron activation.

Table 8. CO_2 and CH_4 in Luther Bog pore water by gas chromatography.

Table 9. Na, Ca, Mg, Al, V, Cr, Mn, Zn and U in Luther Bog pore water by neutron activation.

Table 10. Chloride, sulphate and oxalate in Luther Bog pore water by ion chromatography.

Table 11. GEOCHEM input data.

Table 12. Speciation of metals at pH 4.

Table 13. Speciation of metals at pH 8.

PREFACE

During the summer of 1984 I had the opportunity to study two quite different Sphagnum bogs: the Luther bog north of Guelph, Ontario, and the Barrington bog near Barrington, Nova Scotia. The former is a continental bog underlain by calcareous sediments, the latter is a maritime bog in a siliceous environment; both are ombrotrophic Sphagnum bogs. Aspects of their stratigraphy and inorganic chemistry are presented here but are not discussed in any detail; these are discussed in my dissertation (in preparation).

Since the Luther bog is so close to the well-equipped laboratories of CCIW in Burlington, water analyses were performed on the Luther bog water samples only. Except for some pH measurements, the water analyses reported herein are for samples collected from Luther bog.

Although no fen water samples were collected as part of this study, I wanted to evaluate the effect of pH on metal speciation in peatland waters. To do this I used the same input data as for Luther bog surface water except a pH of 8 instead of 4, and total dissolved Ca of 30 mg l^{-1} rather than 4 mg l^{-1}. These conditions of high pH and Ca are comparable to those of rich fens.

My attempts at speciating metals in peatland surface waters using calculations based on chemical equilibria should be considered a first approximation to a problem which requires greater attention. Caveat: the calculations performed here are only as good as the data used to make them. When more input data

become available, the results of the calculations will more closely approximate reality.

SUMMARY

The geochemistry of two ombrotrophic Sphagnum bogs were compared: the Luther bog north of Guelph, Ontario, and the Barrington bog near Barrington, Nova Scotia. The former is a continental bog underlain by calcareous sediments, the latter is a maritime bog in a siliceous environment. The stratigraphy of the peats (botanical composition, degree of decomposition), and aspects of their inorganic chemistry (ash content, Na, K, Mg, Ca, Al, Fe, Mn, As, Cr, U, W, Zn) are reported.

Ombrotrophic bog surface waters are isolated from local groundwaters. Since they receive no significant inputs of solid (mineral) bases, and contain abundant CO_2 and organic acids, the waters are acidic (approx. pH 4). Accurate pH measurements of bog waters are difficult to perform because of the presence of colloidal and dissolved organic matter, and volatile acids (CO_2, acetic acid, etc.).

The redox chemistry of Luther bog was described by measuring CO_2, CH_4, total dissolved sulphide, and sulphate in the pore waters. The surface pools contain approximately 1 mg l^{-1} SO_4^{2-}. Surface peat pore waters are sulphate-rich: in pore waters above the water table SO_4^{2-} ranges from 2.0 to 16.1 mg l^{-1} and total dissolved sulphide is approximately 10 ug l^{-1}. In the pore waters below the water table SO_4^{2-} ranges from 0.1 to 1.2 mg l^{-1} and total dissolved sulphide is approximately 50 ug l^{-1}. Sulphate accounts for 99 and 95% of the total dissolved inorganic sulphur above and below the water table, respectively. Thus the

Luther bog can be viewed as "oxidizing" with respect to dissolved inorganic sulphur. In pore waters above the water table the CO_2/CH_4 ratios are greater than unity, and are less than unity below it.

In addition to SO_4^{2-}, anions determined by ion chromatography include chloride, oxalate, formate and acetate. Oxalate ranges in concentration from 0.1-0.4 mg l^{-1} and is strongly correlated with SO_4^{2-} ($r = 0.92$, $n = 12$), suggesting a possible redox control. Acetate concentrations are on the order of 0.5 mg l^{-1}. Formate was detected in samples which had been stored @4°C for 10 days, but was not found in fresh samples. In surface water samples the concentrations of metals determined are as follows: Na (0.46 mg l^{-1}), Mg (1.3 mg l^{-1}), Ca (3.7 mg l^{-1}), Al (0.38 mg l^{-1}), V (1 ug l^{-1}), Cr (2 ug l^{-1}), Mn (30 ug l^{-1}), Zn (27 ug l^{-1}), and U (0.4 ug l^{-1}).

In an effort to demonstrate the importance of low molecular weight organic acids on the speciation of dissolved metals, calculations were performed using the computer program GEOCHEM. The data employed in the calculations are from several sources: this study, literature values, and estimated values. Given the input data employed, the calculations show that citrate, oxalate and salicylate complex 50% of the Fe and 20% of the Al at pH 4. The usefulness of these calculations will improve as more input data becomes available.

Methods of pH determination of bog waters require more detailed investigation. The redox chemistry of bog waters can be

further described by measuring the concentrations of individual redox species of interest. To better understand the speciation of dissolved constituents in mire waters we need more data concerning

i) the chemical composition of these waters (Major, trace and ultra trace metals, inorganic and organic ligands), and

ii) the thermodynamic stability of metal-organic complexes.

RÉSUMÉ

On a comparé la géochimie de deux tourbières oligotrophes ombrotrophes à sphaigne : la tourbière Luther au nord de Guelph en Ontario et la tourbière Barrington, située près de Barrington en Nouvelle-Écosse. La première est une tourbière continentale reposant sur des sédiments calcaires et la seconde, une tourbière maritime ayant un environnement siliceux. Le présent article décrit la stratigraphie des tourbes (composition botanique, degré de décomposition) et certains aspects de leur chimie inorganique (teneur en cendres et en Na, K, Mg, Ca, Al, Fe, Mn, As, Cr, U, W, Zn).

Les eaux de surface des tourbières oligotrophes ombrotrophes sont isolées des eaux souterraines locales. Comme elles ne reçoivent aucun apport important de matières solides (minéraux) basiques et qu'elles abondent en CO_2 et en acides organiques, leurseaux sont acides (pH 4 environ). Le pH des eaux de tourbières est difficile à mesurer avec précision à cause de la présence de matières organiques sous forme de colloïdes ou de solutions ainsi que d'acides volatils (CO_2, acide acétique, etc.).

L'oxydoréduction chimique qui a lieu dans la tourbière Luther a été déterminée par dosage du CO_2, du CH_4, du sulfure total dissous et des sulfates dans les eaux de porosité. La teneur en SO_4^{2-} des mares de surface est d'environ 1 $mg.L^{-1}$. L'eau de porosité de la tourbe de surface est riche en sulfates : au-dessus de la surface de saturation, la teneur en SO_4^{2-} varie de 2,0 à 16,1 $mg.L^{-1}$ et celle en sulfure total dissous est d'environ 10 $\mu g.L^{-1}$. Sous la surface de saturation, l'eau de porosité a une teneur en SO_4^{2-} variant entre 0,1 à 1,2 $mg.L^{-1}$ et une teneur en sulfure total dissous d'environ 50 $\mu g.L^{-1}$. Au-dessus et au-dessous de la surface de saturation, les sulfates constituent respectivement 99 et 95 % du soufre inorganique total dissous. En ce qui concerne le soufre inorganique dissous, la tourbière Luther peut donc être considérée "oxydante". Au-dessus de

la surface de saturation, le rapport CO_2/CH_4 est supérieure à l'humidité, alors qu'il est inférieur à l'unité au-delà de cette surface.

En plus de SO_4^{2-}, la chromatographie ionique permet de doser, entre autres, les anions suivants : chlorure, oxalate, formiate et acétate. La concentration d'oxalate varie de 0,1 à 0,4 $mg.L^{-1}$ et elle est fortement liée à la concentration de SO_4^{2-} ($r = 0,92$, $n = 12$), ce qui laisse entrevoir la possibilité d'une régulation par oxydoréduction. Les concentrations d'acétate sont de l'ordre de 0,5 $mg.L^{-1}$. On a décelé du formiate dans des échantillons stockés pendant 10 jours à environ 4 ^{o}C, mais non dans des échantillons frais. Voici les concentrations de métaux trouvées dans des échantillons d'eau de surface : Na (0,46 $mg.L^{-1}$), Mg (1,3 $mg.L^{-1}$), Ca (3,7 $mg.L^{-1}$), Al (0,38 $mg.L^{-1}$), V (1 $\mu g.L^{-1}$), Cr (2 $\mu g.L^{-1}$), Mn (30 $\mu g.L^{-1}$), Zn (27 $\mu g.L^{-1}$) et U (0,4 $\mu g.L^{-1}$).

Pour tenter de démontrer l'importance des acides organiques à faible masse moléculaire dans la formation des espèces métalliques dissoutes, on a effectué des calculs à l'aide du programme GEOCHEM. Les données servant aux calculs ont plusieurs origines : les données de la présente étude, des valeurs trouvées dans la littérature et des valeurs estimatives. Les calculs effectués grâce à ces données d'entrée montrent que les citrates, les oxalates et les salicylates complexent 50 % du Fe et 20 % de l'Al à pH 4. A mesure que de nouvelles données d'entrée se feront jour, l'utilité de ces calculs sera améliorée.

Il est nécessaire d'étudier de façon plus détaillée les méthodes de détermination du pH des eaux de tourbières. Il est possible de mieux décrire la chimie des eaux de tourbières oligotrophes en dosant chacune des espèces des principaux couples redox. Pour mieux comprendre la formation des constituants dissous dans les eaux de fondrières, nous avons besoin de plus de données sur :

1) la composition chimique de ces eaux (principaux métaux, métaux traces et métaux ultratraces, ligands inorganiques et organiques) et

ii) la stabilité thermodynamique des complexes organométalliques.

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I am indebted to George Massis for his patience and skill in helping me collect samples from Luther Bog on many occasions. I thank David Burton for performing all of the gas analyses. Finally, thanks to Lynne Holloway and Shelley McLean for preparing all of the peat samples, performing all of the atomic absorption analyses and ash content determinations.

1.0 INTRODUCTION

Most of the work on inorganic chemistry of peats can be divided into four categories:

1) geochemistry, mainly from the point of view of geochemical exploration for mineral deposits,
2) ecology, mostly in an effort to understand the relationship between the nutrient status of peats and the distribution of living plants in undisturbed mires,
3) soil chemistry, with particular reference to nutrient availability in the "plough layer", and
4) environmental chemistry, using surface peats as monitors of atmospheric metal deposition.

Today there is an increasing interest in peat chemistry because of the potential environmental impact of fuel peat utilization.

Investigations of metal speciation would facilitate a better understanding of metal solubility and bioavailability in peatland ecosystems. Here, peatland waters are analyzed for dissolved metals, inorganic and organic ligands. These data, used in conjunction with data selected from the literature, are used to calculate the distribution of dissolved species using the computer program GEOCHEM.

2.0 OBJECTIVES

The speciation of metals in natural waters can be calculated using a chemical equilibrium computer program such as GEOCHEM. In order for the program to generate meaningful results some fundamental chemical data must be obtained. Here, an emphasis has been placed on

i) major metallic cations,

ii) trace metallic cations,

iii) inorganic ligands,

iv) organic ligands, and

v) dissolved gases.

Using the data generated during the course of this study, and including data from other recent work, the distribution of dissolved species in peatland waters is calculated using GEOCHEM.

Secondary objectives include

i) developing appropriate methods for characterizing the chemistry of bog waters,

ii) outlining some of the problems encountered using these methods and

iii) summarizing the gaps which presently exist in our knowledge of the chemistry of these environments and recommending avenues for further research.

3.0 METHODS

The Luther bog is located within the Luther Marsh Conservation Area, approximately 45 km north of Guelph, Ontario (43°55'N, 80°25'W; see Figure 1). The Barrington bog is located near Barrington, Nova Scotia (43°35'N, 65°30'W; see Figure 2).

3.1 Peat Chemistry

3.1.1 Botanical composition, degree of decomposition and ash content of Luther Bog and Barrington Bog

The botanical composition and degree of decomposition of the peat samples were determined at each naturally occurring change in peat stratigraphy using the field techniques employed by the Geological Survey of Finland and endorsed by the International Peat Society. The major peat types are Sphagnum (S) and Carex (C) and are reported as a percentage of the total peat volume e.g. C5S5-3 represents a peat which is approx. 50% Carex, 50% Sphagnum and 3 on the von Post scale of humification. Minor peat types encountered include shrubby material (N), woody material (L), Eriophorum (ER), Equisetum (EQ), Scheuchzeria (SH) and Trichophorum (TR).

Ash content was determined by ashing approx. 1 g of dry peat in a muffle furance @ 450°C overnight.

3.1.2 Inorganic chemistry of Luther Bog and Barrington Bog

For chemical analyses peat samples were collected at 5 or 10 cm intervals using a steel 10 cm diam. Russian-style auger. Peat

samples were either frozen immediately or kept @ 4°C until they could be prepared for analysis. The samples were dried at 105°C until constant weight, ground using a Wiley mill and stored in 250 ml glass jars which previously had been cleaned in acid.

3.1.2.1 Al, Ca, Mg, Na, K, Fe and Mn by atomic absorption

Approximately 1 g of dry peat was digested using the method of Glooschenko et al. (1980). The precision of these analyses was determined by analyzing 2 sets of 5 replicate samples.

3.1.2.2 Cr, U, Zn, As and W by neutron activation

Approximately 10 g of milled peat was dried at 105°C overnight in acid-washed glass jars and then delivered to X-ray Assay Labs, Don Mills, Ontario, for neutron activation analysis.

3.2 Peat pore water chemistry (Luther Bog)

3.2.1 pH by glass combination electrode

Unfortunately there is no standard method for determining the pH of bog waters. Here, 2 different procedures were employed:

1) direct insertion of a glass combination electrode into wet peat while still in the auger and
2) by measuring the pH of the pore water of these same samples. The pore water was collected by transferring the wet samples to plastic bags and then squeezing the plastic bags. The water was poured from the plastic

bags into small Nalgene bottles and transported in a cooler back to the lab. In the lab these pore waters were vacuum-filtered through a 0.22 um membrane filter and the pH of the resulting solution determined using the same glass combination electrode as above.

3.2.2 CO_2 and CH_4 by gas chromatography

For gas analyses peat cores were collected at 10 cm intervals over the first 100 cm and every 50 cm until the bottom (550 cm) using the Russian-style auger. The peat cores were transferred by hand to plastic bags. The caps of 7 ml Vacutainers (evacuated blood collector tubes) were removed so that 5 ml of the peat pore water could be squeezed into the tube and then recapped. Upon arrival in the laboratory the 2 ml head space was analyzed for CO_2 and CH_4 using gas chromatography.

3.2.3 Al, Ca, Mg, Na, V, Cr, Mn and U by neutron activation

Water samples were collected from 3 zones:

1) in a pit which previously had been dug and allowed to equilibrate with the atmosphere,
2) squeezed from peat in the top 10 cm of the profile and
3) squeezed from peat taken from a depth of 410-450 cm.

Five hundred ml Nalgene bottles and caps were soaked for 2 days in fresh 10% HNO_3 and then rinsed 6 times with distilled water, 3 times with de-ionized distilled water and 6 times with double (glass) distilled water. The bottles were capped tightly,

sealed in plastic bags and taken into the field. Plastic gloves were used while washing the bottles and caps and during sample collection. Peat cores were transferred to plastic bags which were then squeezed to force out the pore water. The bottles were rinsed with sample before filling, capped tight and immediately placed in a cooler for transport back to the lab.

In the lab the water samples were centrifuged in 100 ml Nalgene centrifuge tubes (previously cleaned as outlined above for Nalgene bottles) @ 20,000 Xg for 30 minutes. The supernatant was poured into clean (as outlined above) Nalgene bottles until approx. 250 ml was collected. These were then preserved with 2 ml Ultrex HNO_3 per 1 of sample, capped tight, sealed individually in plastic bags and stored @ 4°C until they could be delivered to XRAL for neutron activation analysis. The samples were delivered to the lab within 3 days of collection.

3.2.4 Chloride, sulphate and oxalate by ion chromatography

For anion analyses peat cores were collected every 5 cm for the first 50 cm and at 120, 220 and 430 cm. The cores were transferred to plastic bags and the bags then squeezed to provide enough water to fill 30 ml Nalgene bottles. The samples were first pre-filtered through cleaned glass fibre filters, filtered through 0.22 um cellulose nitrate membrane filters and stored @ 4°C in 30 ml Nalgene bottles. A Dionex model 2010i ion chromatograph was used to determine chloride, sulphate and oxalate. The operating conditions employed and retention times obtained for

these anions are provided in Table 1.

3.3 Speciation calculations using GEOCHEM

GEOCHEM is a computer program for calculating chemical equilibria in natural waters. It considers complexation, precipitation, oxidation-reduction, cation exchange and metal ion adsorption equilibria for up to 36 metals and 69 ligands. It is described in detail in the GEOCHEM manual (Sposito and Mattigod 1979).

The input data employed in the calculations are shown in Table 11. These data were generated as part of the present study, except where noted.

4.0 RESULTS

4.1 Peat Chemistry

4.1.1 Botanical composition, degree of decomposition and ash content of Luther Bog and Barrington Bog

The botanical composition, degree of decomposition and ash content of the peat samples from Luther Bog are provided in Table 2 and those for Barrington Bog in Table 3.

4.1.2 Inorganic chemistry of Luther Bog and Barringer Bog

Precision has been determined from replicate analyses and is expressed as the estimated mean relative error (%). For the peat samples precision is as follows: Ash 6.8%, Al 4.5%, Ca 36.3%, Mg 6.8%, Na 17.2%, K 8.3%, Fe 5.8%, Mn 3.4%, Cr 8.1%, U 13.8%, and Zn 24.4%.

4.1.2.1 Al, Ca, Mg, Na, K, Fe and Mn by atomic absorption

These data for the Luther Bog peats are provided in Table 4 and for the Barrington Bog peats in Table 5.

4.1.2.2 Cr, U, Zn, As and W by neutron activation

These data for the Luther Bog peats are presented in Table 6 and for the Barrington Bog peats in Table 7.

4.2 Peat pore water chemistry (Luther Bog)

4.2.1 pH by glass combination electrode

The results of the pH determinations through the Luther Bog profile are illustrated in Figure 1.

4.2.2 CO_2 and CH_4 by gas chromatography

The results of the gas analyses of Luther Bog are provided in Table 8. In addition, the approximate location of the water table at the time of sample collection is shown.

4.2.3 Al, Ca, Mg, Na, V, Cr, Mn and U by neutron activation

These analyses of Luther Bog water samples are provided in Table 9. Precision is reported as the standard deviation of 3 surface water samples.

4.2.4 Chloride, sulphate and oxalate by ion chromagraphy

These data for Luther Bog water samples are provided in Table 10.

4.3 Speciation of metals in peatland waters

The results of calculations performed at pH 4, $P_{CO_2} = 10^{-1.5}$ atm are shown in Table 12. Those performed at pH 8, $P_{CO_2} = 10^{-1.5}$ atm are shown in Table 13.

5.0 DISCUSSION

5.1 Physical chemistry of bog waters

5.1.1 pH

Hydrogeochemistry is the key to understanding the acid-base chemistry of peatlands. Groundwaters and surface waters contain varying concentrations of bases which decompose in the presence of acids to form salts:

$$\underset{\text{albite (solid base)}}{NaAlSi_3O_8(s)} + \underset{\text{(acid)}}{H_2CO_3^o} + 9/2\ H_2O \longrightarrow$$

$$Na^+ + \underset{\text{(salt)}}{HCO_3^-} + 2H_4SiO_4^o + 1/2\ \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4(s)}$$

Such weathering reactions are the acid-base reactions which control the pH of natural water systems.

Carbonate minerals weather much faster than silicate minerals

$$\underset{\text{base}}{CaCO_3(s)} + \underset{\text{acid}}{H_2CO_3^o} \longrightarrow \underset{\text{salt}}{Ca^{2+} + 2HCO_3^-}$$

All other things being equal, minerotrophic peatlands in calcareous terrains should be less acidic than those in siliceous environments.

All wetlands, whether ombrotrophic Sphagnum bogs (pH approx. 4) or eutrophic Carex fens (pH approx. 8), contain abundant dissolved acids from the decomposition of plant materials: carbonic acid, $H_2CO_3^o$, and organic acids. The pH of peatland waters is thus controlled by the relative rates of production of H^+ (from decaying organic matter) and supply of bases (from local groundwaters and surface waters).

Fens, marshes and swamps all are intimately associated with groundwaters and surface waters. Thus, H^+ produced via decomposition of organic matter is neutralized by dissolved bases and a relatively high pH can be maintained.

As peat accumulates over time, and the thickness of the peat layer increases, the degree of groundwater influence progressively decreases. Ombrotrophic Sphagnum bogs are entirely rain fed (Gr. ombros = rain shower, trophe = nourishment). Since they receive no significant inputs of bases from groundwaters, the H^+ produced via decomposition is not neutralized. The result: bog waters are acidic.

The low pH (approx. 4) in both Luther and Barrington bog surface waters is due to the absence of groundwater influence. The circumneutral pH in the basal peat pore water at Luther Bog is due to the influence of groundwaters which have interacted with calcareous sediments. The basal peat pore waters at Barrington bog are more acidic (pH 4.5) because of the siliceous terrain.

5.1.2 Redox chemistry

The SO_4^{2-} data for porewaters reflect the redox chemistry of the bog (Table 10). Above the water table SO_4^{2-} ranges from 2.0 to 16.1 mg l^{-1} and below the water table from 0.1-1.2 mg l^{-1}. Pools on the bog surface contain on the order of 1 mg l^{-1} SO_4^{2-}; pore waters at the surface are probably SO_4^{2-}-rich because of decomposition processes.

Does SO_4^{2-} really exist at depth in the bog, or is the measured SO_4^{2-} an artefact of dissolved sulphide oxidation during sample collection and preparation? This question was addressed after the present study was officially completed and so is only discussed briefly here. Polyethylene bottles to which a few drops of 2N Zn acetate had been added were used to collect peat pore water samples from surface pools and from a depth of 350-550 cm. The Zn acetate preserves dissolved sulphide and any SO_4^{2-} measured in the sample must also have existed in the bog. Sulphate was again determined using ion chromatography and total dissolved sulphide measured colorimetrically following an acid dissolution.

The pore waters from 350-550 cm below the bog surface were found to contain approximately 1 mg l^{-1} SO_4^{2-}. In the surface pools total dissolved sulphide is on the order of 10 ug l^{-1} and at 350-550 cm it is approx. 50 ug l^{-1}. Thus, in the surface peats, 99% of the total (dissolved) inorganic sulphur is in the sulphate form; in the basal peat pore waters, 95% is sulphate.

In general it is assumed that peat bog waters are "reducing"

below the water table. Clearly, this is not the case, at least not for sulphur in the basal peat pore water at Luther bog. Other workers have found that 90% of the dissolved inorganic sulphur in bog pore waters is sulphate sulphur (Wieder, 1982). The basal peat layer at Luther bog is poorly decomposed (H3) sedge peat, thus the hydraulic conductivity is relatively high. Some shallow groundwaters contain measurable dissolved oxygen (Freeze and Cherry, 1979). Groundwaters containing even traces of dissolved oxygen would make the basal peat layer unsuitable for obligate anaerobic microorganisms, for example, sulphate reducers.

It is entirely possible that the surface and basal peat layers both are "oxidizing", and the middle layers "reducing" with respect to sulphate. Puustjarvi (1952) was probably the first to suggest that this may be true for some mires. This has been difficult to demonstrate at Luther bog because the peats in the middle of the bog profile are well decomposed, making it almost impossible to collect pore water samples.

Since pH, SO_4^{2-}, total dissolved sulphide, P_{CO_2} and P_{CH_4} all have been measured, a quantitative description of the redox chemistry can be obtained by calculating the chemical oxygen potential (P_{O_2}) from

$$SO_4^{2-} + 2H^+ \longrightarrow H_2S^o + 4O_2(g)$$

or

$$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$$

and then Eh from

$$\log(P_{O_2}) = 67.57\ Eh + 4\ pH - 83.12$$

A more detailed discussion of the redox chemistry of bog waters is provided elsewhere (Shotyk, thesis). In general, for groundwater samples, there is a lack of internal equilibrium amongst redox couples; this problem and its implications are discussed in detail by Lindberg and Runnells (1984).

5.2 Chemical composition of surface waters and pore waters

5.2.1 Dissolved metals

The major element data (Na, Mg, Ca) presented here are comparable to those of other bogs (for example Witting, 1947). According to Heinselman (1970) ombrotrophic waters contain less than 2.8 ppm Ca whereas the surface water at Luther bog contains 3.7 $\pm$ 0.2 ppm. Although it is possible that the surface of Luther bog is slightly minerotrophic, it is much more likely that the dust supplied to the bog is Ca-rich.

There are few reliable trace metal analyses of bog waters available for comparison. The Mn data are comparable to those of Swedish bog waters (Witting, 1947). The other trace elements are well within the ranges reported for freshwaters (Bowen, 1979).

5.2.2 Organic acids

By using a borate rather than a carbonate elvent, acetic and formic acids can be determined using ion chromatography. Since much of the acetic acid is lost during vacuum filtration, analyses were made on fresh, raw (ie. unfiltered) samples. Under these conditions 0.5 mg l^{-1} acetic acid was commonly found. In addition, in filtered samples which had been stored for 10 days @ 4°C up to 1.0 mg l^{-1} formic acid was found. This acid could not be detected in fresh samples so its presence in the stored samples may be due to decomposition of the dissolved organic matter. Clearly, the abundance of low molecular weight organic acids in bog waters needs to be further investigated.

Oxalic acid was found to range from 0.1-0.4 mg l^{-1} (Table 10); it correlates well with SO_4^{2-} ($r = 0.92$), suggesting a possible redox control on its concentration. Since oxalic acid is a relatively strong organic acid (in terms of its dissociation constants; $pK_{A_1} = 1.3$, $pK_{A_2} = 3.9$), it must contribute to the low pH of these waters. Other low molecular weight organic acids, for example citric, glutaric, fumaric, malonic, succinic etc., are probably important as well.

Oxalic acid forms stable complexes with many metals, this is discussed further below.

5.3 Speciation of dissolved constituents

5.3.1 pH

The differences in speciation between pH 4 and 8 are clear

(Tables 12 and 13). At pH 4, dissolved metals must compete with protons for organic ligands; at pH 8, organic ligands must compete for metals with hydroxo and carbonate ligands.

Small differences in pH can have a great effect on metal speciation, especially at the low pH range where small differences in pH correspond to large differences in H^+ activity. For example, calculations performed at pH 3.9 and pH 4.2 yield very different results (not shown). This fact illustrates the need for accurate pH measurements for speciation calculations.

Some of the problems encountered in measuring the pH of bog waters are described in this study. Until an accurate method of pH determination is developed for carbon-rich waters, uncertainties concerning pH will be one of the greatest limitations of speciation calculations.

5.3.2 Redox chemistry

No redox reactions are considered in the speciation calculations performed here. Few natural water systems maintain internal equilibrium amongst redox couples (Lindberg and Runnells, 1984). Thus, using Eh as a master variable in GEOCHEM offers no particular advantage. In the present study the surface waters are assumed to be oxidizing with respect to Cu, Fe and U. For example, Fe(III) is assumed to be equal to total dissolved iron.

5.3.3 Dissolved metals

Some of the metal concentrations employed in the calculations are from reports published in the journal literature, or are "educated guesses", for example, $Cu_T = Zn_T$. The concentrations of many trace metals can be varied over an order of magnitude without significantly affecting the distribution of species. The estimates employed are helpful in producing a first approximation to the speciation problem.

As more metal concentration data becomes available, the accuracy of such calculations will improve. Soft acid metals such as Ag, Cd and Hg are especially important because they form stable organic complexes, thereby affecting the availability of organic ligands for other metals.

5.3.4 Organic ligands

At pH 4 citric, oxalic and salicylic acids complex more than 50% of the total dissolved Fe. At the same pH almost 20% of the Al is organically-found. Recall the caveat announced in the Preface: the calculations performed here are only as good as the data used to make them. It is possible that all of the dissolved Fe and Al in bog surface waters is in organic combination. However, it is difficult to demonstrate this using GEOCHEM (and similar computer programs) because of the paucity of data concerning

i) the abundance of low molecular weight organic acids in peatland waters, and

ii) the thermodynamic stability of metal-organic complexes. These are probably the greatest limitations to the speciation calculations.

Some organic complexes of metals are extremely stable, for example the glycine complex of Pd and the p-aminosalicylic acid complex of U. However, in order to evaluate the effect of an individual ligand, one must consider its interactions with all of the potentially important metals, not just the metal of interest. Computer programs for calculating chemical speciation are unquestionably useful. However, until additional basic information is made available, it appears that "the Emperor has no clothes".

5.3.5 Inorganic ligands

Total dissolved sulphide in Luther bog waters was determined after the present report was completed, and its effect on metal speciation is discussed in detail elsewhere (Shotyk, thesis).

At pH 8, carbonate complexes of Cr, Cu, Fe, Ni, Pb, U and Zn apparently are very important. This observation must be considered carefully because

i) very few organic acids have been considered in the calculations, and

ii) it is not immediately apparent to the writer the source of thermodynamic stability constants of carbonate complexes of these metals; the values may be estimates rather than actual measured values.

It is possible that the role of carbonate complexes has been overemphasized.

Fluoride is a potentially important ligand for both Al and U. Until values for F^- concentration are available for peatland waters, the relative importance of this ligand will remain uncertain.

Phosphate also may be an important ligand, particularly for Cr and U. Data for PO_4^{3-} concentration in peatland waters are rare, and the value employed here is an estimate.

6.0 CONCLUSIONS

6.1 pH

Inputs of solid (mineral) bases to bog surface waters are negligible. In the absence of these bases, carbonic acid and organic acids produced via decomposition render bog waters acidic.

The pH profile at Luther bog increases from approximately 4 at the surface to approximately 7 at depth, reflecting the change from ombrotrophic to minerotrophic conditions. The pore waters of the minerotrophic basal peats are enriched in bases ($CaCO_3$) from local calcareous sediments, hence the circumneutral pH. The Barrington bog, developed in a siliceous terrain, is almost uniformly acidic with depth.

Accurate pH measurements in bog waters are difficult to perform because

i) volatile inorganic and organic acids are abundant, and may be lost during sample collection, preparation and analysis,

ii) dissolved and colloidal organic substances are also abundant, and tend to lower the apparent pH, and

iii) dissolved, chemically reduced sulphur species may become oxidized upon sample collection, preparation and analysis.

6.2 Redox chemistry

The sulphate profile in pore waters through Luther bog reflects the change from aerobic conditions above the water table to anaerobic conditions below. Even in the basal peats, however, there is still measurable sulphate. In fact, 95-99% of the total dissolved inorganic sulphur is sulphate. The permeable, minerotrophic basal peats may contain traces of dissolved oxygen from local groundwaters, rendering the environment unsuitable for sulphate reducing bacteria.

6.3 Speciation of dissolved constituents

Oxalic acid in bog waters ranges from 0.1-0.4 mg l^{-1}. This acid must contribute to the low pH of bog surface waters and is an effective complexing agent for dissolved metals. Numerous other low molecular weight organic acids, for example salicylic, citric, tartaric etc., are probably equally as important.

7.0 RECOMMENDATIONS FOR FURTHER STUDY

7.1 Physical chemistry of peatland waters

7.1.1 pH

Despite their apparent simplicity, accurate pH measurements are no small task. The problems inherent in bog water samples are discussed above. Innovative methods of pH measurement need to be explored. For example, peat samples could be collected in the field and immediately transported to the lab under an N_2 atmosphere in a glove box. In the laboratory the pore water could be extracted using a membrane-type gas-driven sediment squeezer through a 0.45 or 0.2u m membrane filter. Analyses of the sample would be performed in the glove box. Such a procedure would circumvent the problems of losses of volatile acids, oxidation of dissolved sulphides, and the effect of colloids.

7.1.2 Redox chemistry

Measurements of Eh in bog waters would be difficult because dissolved sulphides and organic substances may poison the Pt electrode. Interpreting Eh measurements is even more difficult. In most groundwater environments there is no internal equilibrium amongst the various redox couples. Rather than measure Eh, the individual redox species of interest should be determined (Lindberg and Runnells, 1984).

7.2 Chemical composition of peatland waters

7.2.1 Dissolved metals

The major element chemistry (Na, K, Mg, Ca) of peatland waters is fairly well established. See, for example, Witting (1947) or Heinselman (1970). The trace element chemistry (Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) of these waters has received very little attention. Data concerning the abundance of ultra-trace metals (Mo, Ag, Cd, Au, Hg, Pb and the platinum group metals) are almost completely lacking.

7.2.2 Inorganic ligands

The fluoride and phosphate concentrations employed in the speciation calculations performed here are estimates; these potentially important ligands require further attention.

Other inorganic ligands, for example, Br^-, I^-, CN^-, SCN^-, are potentially important, especially for soft acid metals such as Cd, Pb and Hg.

Numerous anions can be determined using ion chromatography. For future studies an MPIC-NG-1 guard column is recommended: it will remove the hydrophobic organic materials which are present in bog waters, and can be cleaned with 90% methanol. The HPIC-AG-4 guard column employed in the present study was extremely difficult to clean and solutions greater than 15% methanol would cause bead swelling. Also, an AS-3 separator column is recommended; because of its greater bead size relative to the AS-4, it should be less prone to clogging.

7.2.3 Organic ligands

Low molecular weight organic acids are relatively abundant in bog waters; they contribute to the low pH and affect metal speciation. This is one of the first reports of individual organic acids in peatland waters. Further studies are necessary to quantitatively identify such acids in bog waters. Ion chromatography exclusion (ICE) can be used to determine these acids: acetic, formic, propionic, butyric, lactic, maleic, malonic, oxalic, succinic, tartaric, pyruvic, benzoic, adipic, citric and fumaric.

7.3 Speciation of dissolved constituents

There are now more than 100 computer programs for calculating chemical speciation in natural waters. The results of such calculations can be no better than the data used to obtain them. Clearly, what is needed now is more data concerning

i) the chemical composition of natural waters (major, trace and ultra-trace metals, inorganic and organic ligands), and

ii) the thermodynamic stability constants of metal-organic complexes.

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9.0 FIGURES

Figure 1. Location of Luther bog, Ontario.

Figure 2. Location of Barrington bog, Nova Scotia.

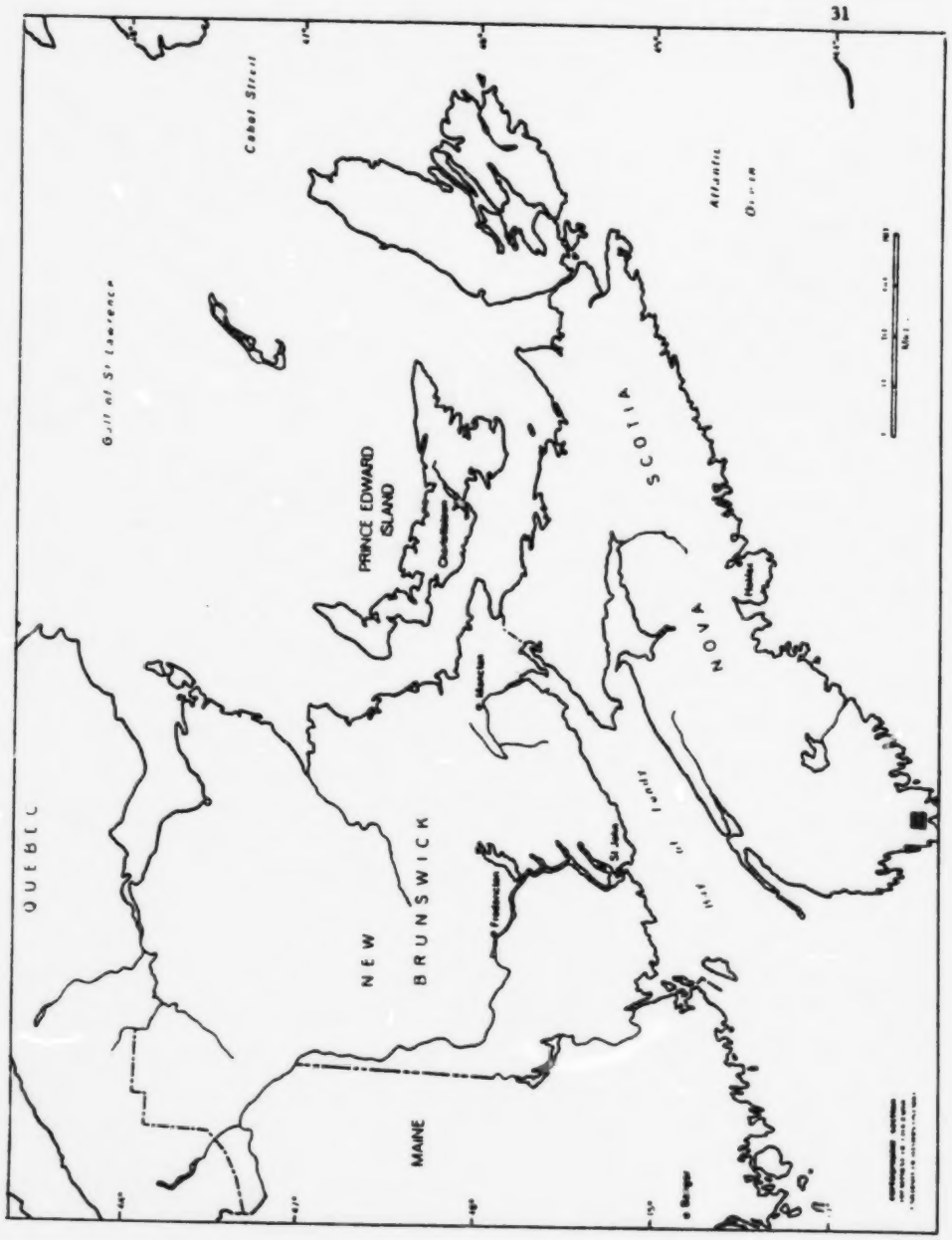
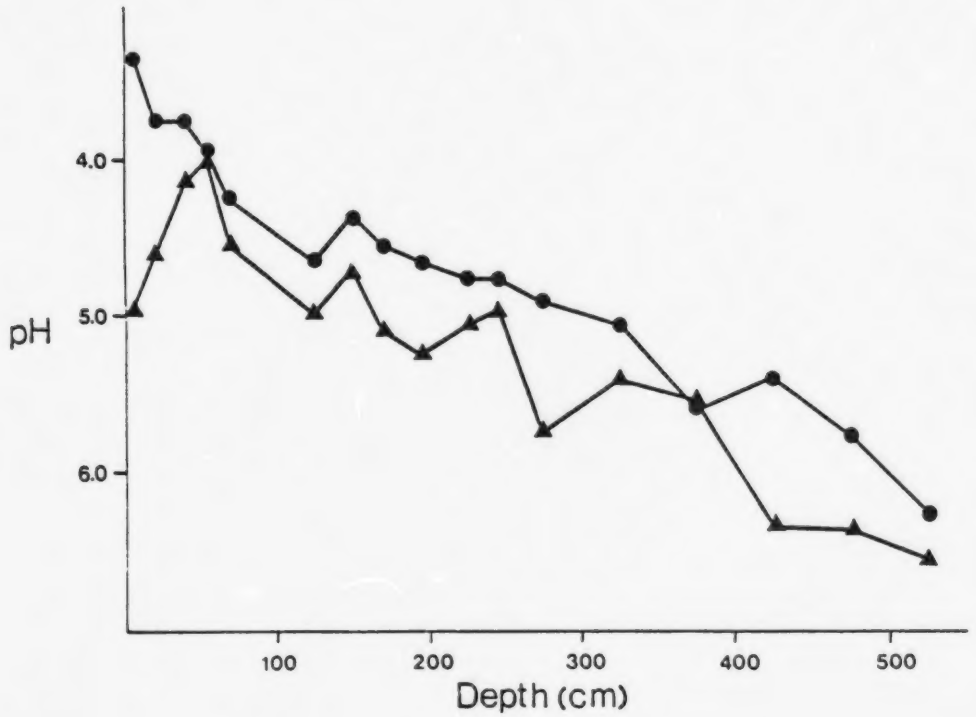


Figure 3. pH determination by direct insertion of glass combination electrode into wet peat (●) and by vacuum filtering (0.22 μm) pore water squeezed from the same samples (▲).



10.0 TABLES

Table 1. Operating conditions employed for Dionex model 2010i ion chromatograph.

Dionex Model 2010i Ion Chromatograph

- HPIC S-4 Separator Column
- HPIC AG-4 Guard Column
- Flow rate 2.0 ml min^{-1}
- Temperature Compensation 1.7
- Chart speed 20 cm/hr

Anion	Eluent	Output Range (uS)	Retention Time (min)
Cl^-	0.003 M $NaHCO_3$+0.00224 M Na_2CO_3	10	1.5
SO_4^{2-}	"	"	5.6
OX^{2-}	"	1	7.5
$ACET^-$	0.0025 M $Na_2B_4O_7$-$10H_2O$	1	1.8
$FORM^-$	"	1	2.4

Table 2. Botanical composition, degree of decomposition and ash content of peat samples from Luther Bog.

Depth (cm)	Peat Type and H	Ash Content (%)*
0-10	S0-3	11.5
10-30	S8N2-3	3.6
30-50	S0-3	1.5
50-60	S0-6	1.9
60-80	S9ER1-7	2.3
80-110	S9ER1-8	3.4
110-140	S0-4	1.6
140-160	S9ER1-8	2.4
160-180	S0-4	2.1
180-210	S9SH1-5	2.6
210-240	S8SH2-5	3.6
240-250	S5SH4N1-4	3.2
250-350	C8SH2-5	5.1
350-400	C7SH3-4	6.7
400-500	C6SH4-3	5.2
500-550	C6SH4-4	5.7
550-630	algal gyttja	25.1
630+	clay	-

* samples were collected at 10 cm intervals.
Results presented here are mean values for the interval shown
e.g. ash content of 30-50 cm

$$\frac{\text{ash (30-40cm)} + \text{ash (40-50cm)}}{2}$$

Table 3. Botanical composition, degree of decomposition and ash content of peat samples from Barrington Bog.

Depth (cm)	Peat Type and H	Ash Content*(%)
0-10	NITR2S7-5	3.4
10-100	TR3S7-4	1.8
100-110	TR2S8-6	1.5
110-140	TR2S8-5	1.7
140-160	TR2S8-4	1.6
160-180	TR2S8-7	1.4
180-210	NITRIS8-3	1.1
210-220	TRIS9-7	1.5
220-230	EQIS9-4	1.6
230-240	NIEQIS8-6	2.3
240-300	NIS9-8	4.3
300+	rock	-

* see Table 2

Table 4. Al, Ca, Mg, Na, K, Fe and Mn in Luther Bog peat samples by atomic absorption.

	Luther Bog						
Depth (cm)	Al	Ca	Mg	Na	K	Fe	Mn
0-10	3385.2	1288.7	427.8	105.8	493.0	3069.2	39.6
10-20	1962.5	112.5	389.0	87.5	266.5	776.5	7.0
20-30	1279.8	1018.9	440.4	53.7	117.3	478.1	4.0
30-40	763.3	1764.3	542.5	70.6	69.1	468.5	3.5
40-50	827.5	1404.2	435.8	77.2	84.3	438.3	3.5
50-60	712.5	850.0	318.5	84.5	60.0	417.5	3.5
60-70	852.6	927.8	286.4	107.8	63.2	417.3	3.0
70-80	1318.4	821.0	218.4	107.0	82.1	391.5	3.0
80-90	1837.5	374.6	221.3	86.4	87.9	420.1	3.0
90-100	1706.8	514.6	240.0	74.3	77.3	378.5	2.0
150-160	1152.3	2868.2	372.7	103.7	70.1	446.4	2.5
200-210	1540.6	6387.8	403.3	116.2	79.2	472.9	3.0
250-260	1548.5	17357.6	609.4	132.4	110.4	946.1	7.5
300-310	1962.5	19250.0	620.0	151.0	140.0	1203.5	10.5
350-360	2744.5	25074.9	683.6	101.8	359.8	1691.6	18.0
400-410	1312.5	22500.0	615.0	122.0	131.5	1710.0	2.5
450-460	1492.5	211.4	517.4	89.5	149.8	1781.1	27.9
500-510	910.7	274.5	504.0	98.8	110.3	2080.8	40.4
580-590	5104.6	7096.6	1220.1	140.9	1738.0	12549.8	60.3

Table 5. Al, Ca, Mg, Na K, Fe and Mn in Barrington Bog peat samples by atomic absorption.

	Barrington Bog ppm						
Depth (cm)	Al	Ca	Mg	Na	K	Fe	Mn
0-10	925.9	1238.7	1876.9	366.9	1626.6	993.0	84.6
10-20	400.8	839.2	1658.3	347.2	137.8	358.7	4.0
20-30	300.0	537.5	1445.0	313.0	104.5	211.5	2.0
30-40	461.6	548.9	1571.9	364.8	138.7	280.4	2.0
40-50	437.5	562.5	1505.0	370.5	142.5	298.0	2.0
50-60	474.5	487.0	1468.5	364.1	131.4	291.2	2.0
60-70	501.0	313.1	1442.9	372.7	125.3	300.6	2.0
70-80	538.0	450.5	1531.5	324.3	132.1	292.8	2.0
80-90	559.7	522.4	1552.2	332.8	131.8	296.5	2.0
90-100	524.0	474.1	1472.1	362.8	132.2	294.4	2.0
100-110	736.8	462.0	1643.4	361.1	162.8	295.7	1.5
110-120	574.4	474.5	1728.3	365.1	153.3	307.7	1.0
120-130	561.4	823.4	1936.1	432.1	163.7	342.8	1.5
130-140	611.9	1011.5	2077.9	418.1	170.8	395.6	1.5
140-150	429.3	1363.9	2137.1	411.9	154.2	393.4	1.5
150-160	362.1	1348.7	2003.0	397.1	154.8	453.0	2.0
160-170	524.5	999.0	1678.3	361.6	167.8	451.5	2.5
170-180	387.9	813.3	1256.3	355.9	130.1	418.4	2.5
180-190	DNA						
190-200	436.6	110.3	1526.9	337.3	132.7	497.5	3.5
200-210	399.2	1210.1	1507.0	348.3	122.3	506.0	4.5
210-220	675.0	1087.5	1365.0	346.0	125.0	618.0	5.5
220-230	812.5	1700.0	1635.0	363.0	131.0	819.0	7.0
230-240	1200.0	1450.0	1520.0	308.5	135.5	943.0	8.5
240-250	1948.1	849.2	1308.7	325.7	182.8	981.5	9.0
250-260	2736.3	510.0	1114.4	371.6	181.6	1065.7	13.9
260-270	DNA						
270-280	4000.0	237.5	930.0	313.5	257.5	1107.0	14.0
280-290	4611.2	162.0	702.9	303.6	236.8	995.0	9.0
290-300	6112.8	12.5	294.4	247.5	211.1	614.3	9.0

Table 6. Cr, U, Zn, As and W in Luther Bog peat samples by neutron activation.

	Luther Bog				
			ppm		
Depth (cm)	Cr	U	Zn	As	W
0-5	12.0	0.38	46	7.80	0.47
5-10	2.9	0.20	29	3.20	0.26
10-15	2.3	0.16	30	2.10	0.21
15-20	1.6	0.08	27	1.20	0.05
20-25	1.5	0.90	23	0.89	0.07
25-30	1.0	0.07	16	0.73	0.07
30-35	1.1	0.06	12	0.43	0.03
35-40	1.1	0.07	8	0.32	0.05
40-45	1.1	0.07	6	0.34	0.09
45-50	0.9	0.03	6	0.24	0.05
50-55	1.5	0.06	7	0.59	0.05
55-60	1.1	0.05	4	0.33	0.07
60-65	1.5	0.09	5	0.37	0.10
65-70	1.8	0.13	7	0.37	0.12
70-75	1.5	0.13	9	0.35	0.06
75-80	2.5	0.20	4	0.35	0.10
80-85	2.4	0.19	3	0.41	0.21
85-90	2.3	0.15	2	0.31	0.12
90-95	1.6	0.14	<2	0.31	0.13
95-100	1.3	0.06	2	0.39	0.03
150-160	1.5	0.11	5	0.38	0.06
200-210	2.1	0.09	3	0.26	0.10
250-260	2.0	0.09	3	0.54	0.07
300-310	1.9	0.10	3	0.63	0.14
350-360	4.6	0.22	4	0.96	<1.00
400-410	1.8	0.09	3	0.93	0.08
450-460	1.0	0.05	4	0.86	0.10
500-510	1.5	0.09	5	1.30	<1.00
580-590	18.0	6.50	130	6.00	0.80

Table 7. Cr, U, Zn, As and W in Barrington Bog peat samples by neutron activation.

	Barrington Bog ppm				
Depth (cm)	Cr	U	Zn	As	W
0-10	2.9	0.06	36	3.80	0.11
10-20	0.8	0.03	8	1.70	0.45
20-30	1.1	0.05	5	1.50	0.16
30-40	1.0	0.04	7	0.23	0.28
40-50	0.7	0.09	6	0.78	0.31
50-60	0.8	0.06	5	0.75	0.10
60-70	0.6	0.09	7	0.25	0.50
70-80	1.1	0.22	5	0.30	<0.30
80-90	1.2	0.08	8	0.50	<1.00
90-100	0.8	0.07	5	0.65	0.28
100-110	1.2	0.09	5	0.50	0.27
150-160	0.6	0.07	<2	<0.20	<1.00
200-210	0.8	0.04	<2	0.13	<0.05
250-260	2.3	1.50	4	1.30	0.20

Table 8. CO_2 and CH_4 in Luther Bog pore water by gas chromatography.

Depth (cm)	CO_2(%)*	CH_4(%)*	CO_2/CH_4
0-10	1.89	0.36	5.3
10-20	1.90	0.32	5.9
20-30	1.58	0.58	2.7
30-40	1.67	0.63	2.7
40-50	2.16	1.49	1.5
	water table (50 cm)		
110-140	3.05	3.65	0.8
180-210	3.81	5.55	0.7
210-240	4.12	6.47	0.6
250-300	3.95	5.37	0.7
300-350	5.40	8.28	0.7
350-400	5.32	7.49	0.7
400-450	4.71	6.19	0.8
450-500	5.57	8.60	0.7
500-550	4.87	7.73	0.6

* mean of 2 or 3 analyses

Table 9. Na, Ca, Mg, Al, V, Cr, Mn, Zn and U in Luther Bog pore water by neutron activation.

Metal	Surface	0-10 cm	410-450 cm
Na	460 ± 40 ppb	680	550
Ca	3.7 ± 0.2 ppm	4.3	30.0
Mg	1.30 ± 0.16 ppm	1.30	1.20
Al	380 ± 20 ppb	530	130
V	1.2 ± 0.4 ppb	1.9	0.3
Cr	2 ± 0 ppb	2	<2
Mn	30 ± 3 ppb	6	27
Zn	27 ± 5 ppb	50	2
U	0.4 ± 0.05 ppb	0.3	0.3

Table 10. Chloride, sulphate and oxalate in Luther Bog pore water by ion chromatography.

Depth (cm)	SO_4^{2-} (mg ℓ^{-1})	Cl^- (mg ℓ^{-1})	OX^{2-} (mg ℓ^{-1})
0-5	16.1	0.7	0.4
5-10	16.1	0.3	0.4
10-15	10.4	0.3	0.2
15-20	5.6	0.3	0.2
20-25	5.9	0.3	0.2
25-30	2.0	0.7	0.1
	water table (30 cm)		
30-35	1.2	0.4	0.2
35-40	0.5	0.5	0.1
40-45	0.3	0.6	0.1
45-50	0.9	0.6	0.1
120-130	0.5	0.6	0.1
220-230	0.5	0.6	0.1
430-450	0.1	0.3	0.1

Table 11. GEOCHEM input data.

Species	Concentration (ug l^{-1} except where noted)	-log concentration (mol l^{-1})	source
Ca^{2+}	3.7 mg l^{-1} (pH4)	4.03	1
	30.0 mg l^{-1} (pH8)	3.13	1
Mg^{2+}	1.3 mg l^{-1}	4.27	1
K^{+}	0.5 mg l^{-1}	4.89	2
Na^{+}	0.5 mg l^{-1}	4.66	1
Al^{3+}	0.4 mg l^{-1}	5.05	1
Fe^{3+}	0.5 mg l^{-1}	6.26	2
Mn^{2+}	30	6.33	1
Cu^{2+}	30	6.33	3
Zn^{2+}	30	6.34	1
Ni^{2+}	30	7.50	3
Cr^{3+}	2	7.41	1
Pb^{2+}	3	7.84	4
UO_2^{2+}	0.5	8.68	1
SO_4^{2-}	1000	4.99	1
Cl^{-}	300	5.08	1
F^{-}	10	6.28	4
NH_3	30	5.79	5
PO_4^{3-}	150	5.77	6
$acetate^{-}$	500	5.08	1
$formate^{-}$	500	4.96	1
$oxalate^{2-}$	500	5.26	1
$citrate^{3-}$	500	5.58	7
$tartrate^{2-}$	500	5.48	7
$maleate^{2-}$	500	5.48	7
$salicylate^{2-}$	500	5.44	7
$glycinate^{-}$	7.7	6.99	8
$glutamate^{2-}$	3.7	7.60	8
$cysteine^{2-}$	0.1	9.00	9
$ornithine^{-}$	0.1	9.12	8
$lysine^{-}$	1.5	7.99	8
$aspartate^{-}$	5.1	7.42	8
$serine^{-}$	12.5	6.93	9

alanine$^-$	9.8	6.96	8
tyrosine^{2-}	0.8	8.36	8
methionine$^-$	0.1	9.17	8
phenylalanine$^-$	9.1	7.26	8
leucine$^-$	7.5	7.24	8
proline$^-$	0.7	8.22	8

Sources

1. this study
2. Verry (1975)
3. assume $[Cu]_T = [Zn]_T$ and $[Ni]_T = [Cr]_T$
4. estimated by ion chromatography. A borate eluent was used to separate acetate, formate and flouride (0.0025 M $Na_2B_4O_7$). Actual value may be lower
5. calculated from NH_4^+ of Hemond (1980)
6. an upper limit. Bog waters have been found to contain PO_4^{3-} in concentrations below this limit of detection (Gorham et al., 1985)
7. assume $[citrate]_T$, $[tartrate]_T$, $[maleate]_T$, $[salicylate]_T = [oxalate]_T$
8. from free, dissolved amino acids in "muskeg leachate" (Baker et al., 1982)
9. estimate

Table 12. Speciation of metals at pH 4.

Ca	
as a free metal/	99.8 percent
bound with SO_4/	.1 percent
Mg	
as a free metal/	99.9 percent
K	
as a free metal/	100.0 percent
Na	
as a free metal/	100.0 percent
Fe(III)	
as a free metal/	.3 percent
bound with CO_3	2.5 percent
bound with PO_4	1.4 percent
bound with cit/	4.9 percent
bound with ox/	34.2 percent
bound with sal/	14.6 percent
bound with OH/	42.1 percent
Mn	
as a free metal/	99.8 percent
bound with SO_4/	.1 percent
CU(II)	
as a free metal/	91.6 percent
bound with CO_3/	6.0 percent
bound with SO_4/	.1 percent
bound with ox/	1.3 percent
bound with tart/	.9 percent
Zn	
as a free metal/	99.3 percent
bound with CO_3/	.2 percent
bound with SO_4/	.1 percent
bound with ox/	.2 percent
bound with tart/	.1 percent
Ni	
as a free metal/	99.0 percent
bound with CO_3/	.4 percent
bound with SO_4/	.1 percent
bound with ox/	.4 percent
Pb	
as a free metal/	94.6 percent
bound with CO_3/	1.6 percent
bound with SO_4/	.2 percent
bound with tart/	3.5 percent

Cr		
	as a free metal/	2.2 percent
	bound with CO_3/	91.7 percent
	bound with PO_4/	3.9 percent
	bound with ox/	.5 percent
	bound with OH/	1.6 percent
Al		
	as a free metal/	72.8 percent
	bound with SO_4/	.5 percent
	bound with F/	3.5 percent
	bound with cit/	14.8 percent
	bound with ox/	2.5 percent
	bound with sal/	.1 percent
	bound with OH/	5.7 percent
UO_2		
	as a free metal/	90.3 percent
	bound with SO_4/	.5 percent
	bound with cit/	2.9 percent
	bound with ox/	1.6 percent
	bound with sal/	.7 percent
	bound with OH/	3.8 percent
CO_3		
	bound with H/	100.0 percent
SO_4		
	as a free ligand/	97.1 percent
	bound with Ca/	1.0 percent
	bound with Mg/	.4 percent
	bound with Al/	.7 percent
	bound with H/	.7 percent
Cl		
	as a free ligand/	99.9 percent
F		
	as a free ligand/	1.4 percent
	bound with Al/	98.4 percent
	bound with H/	.1 percent
NH_3		
	bound with H/	100.0 percent
PO_4		
	bound with Ca/	.2 percent
	bound with Mg/	.1 percent
	bound with Fe/	7.5 percent
	bound with H/	92.1 percent

Ac	
as a free ligand/	15.4 percent
bound with H/	84.6 percent
Cit	
bound with Fe_3/	16.7 percent
bound with Al/	83.3 percent
Ox	
as a free ligand/	2.8 percent
bound with Ca/	.8 percent
bound with Fe/	78.7 percent
bound with Cu/	.1 percent
bound with Al/	13.6 percent
bound with H/	3.9 percent
Sal	
bound with Fe/	35.8 percent
bound with Al/	.5 percent
bound with H/	63.6 percent
Tart	
as a free ligand/	26.4 percent
bound with Ca/	.9 percent
bound with Mg/	.2 percent
bound with Cu_2/	.1 percent
bound with H/	72.3 percent
Gly	
bound with Fe_3/	.2 percent
bound with H/	99.8 percent
Glut	
bound with H/	100.0 percent
Cyst	
bound with H/	100.0 percent
Orn	
bound with H/	99.9 percent
Lys	
bound with H/	100.0 percent
Asp	
bound with Fe/	5.0 percent
bound with H/	95.0 percent
Ser	
bound with Fe/	.1 percent
bound with H/	99.9 percent

Ala	
bound with Fe/	.3 percent
bound with H/	99.7 percent
Tyr	
bound with H/	100.0 percent
Met	
bound with H/	100.0 percent
Phe	
bound with H/	99.9 percent
Leu	
bound with Fe/	.2 percent
bound with H/	99.8 percent
Pro	
bound with H/	100.0 percent
HVO_4	
bound with H/	100.0 percent
Mal	
as a free ligand/	.7 percent
bound with H/	99.3 percent
For	
as a free ligand/	69.4 percent
bound with Ca/	.1 percent
bound with H/	30.3 percent

Table 13. Speciation of metals at pH 8.

Ca	
as a free metal/	97.1 percent
bound with CO_3/	1.4 percent
bound with SO_4/	.1 percent
bound with ox/	1.2 percent
bound with tart/	.1 percent
Mg	
as a free metal/	98.6 percent
bound with CO_3/	1.0 percent
bound with ox/	.2 percent
K	
as a free metal/	99.9 percent
Na	
as a free metal/	99.9 percent
bound with CO_3/	.1 percent
Fe(III)	
bound with CO_3/	99.8 percent
bound with OH/	.2 percent
Mn	
as a free metal/	84.1 percent
bound with CO_3/	14.8 percent
bound with PO_4/	.3 percent
bound with ox/	.4 percent
bound with OH/	.2 percent
Cu(II)	
as a free metal/	2.8 percent
bound with CO_3/	85.2 percent
bound with NH_3/	.3 percent
bound with PO_4/	.8 percent
bound with ox/	1.2 percent
bound with sal/	.6 percent
bound with gly/	1.4 percent
bound with glut/	.4 percent
bound with asp/	1.2 percent
bound with ser/	.3 percent
bound with ala/	1.5 percent
bound with phe/	.9 percent
bound with leu/	1.0 percent
bound with OH/	2.4 percent
Zn	
as a free metal/	52.4 percent
bound with CO_3/	34.2 percent
bound with PO_4/	.3 percent
bound with ox/	2.6 percent
bound with tart/	.3 percent

bound with cyst/	.1 percent
bound with OH/	9.7 percent
Ni	
as a free metal/	23.9 percent
bound with CO_3/	71.6 percent
bound with PO_4/	.3 percent
bound with ox/	2.9 percent
bound with asp/	.5 percent
bound with ser/	.2 percent
bound with ala/	.1 percent
bound with OH/	.3 percent
Pb	
as a free metal/	2.4 percent
bound with CO_3/	91.2 percent
bound with PO_4/	.1 percent
bound with tart/	.3 percent
bound with cyst/	1.6 percent
bound with OH/	4.2 percent
Cr	
bound with CO_3/	100.0 percent
Al	
bound with cit/	17.8 percent
bound with OH/	82.2 percent
UO_2	
bound with CO_3/	100.0 percent
CO_3	
as a free ligand/	.6 percent
bound with Ca/	.1 percent
bound with Fe /	2.7 percent
bound with H/	96.5 percent
SO_4	
as a free ligand/	98.6 percent
bound with Ca/	1.0 percent
bound with Mg/	.4 percent
Cl	
as a free ligand/	100.0 percent
F	
as a free ligand/	99.7 percent
bound with Mg/	.2 percent

NH_3		
	as a free ligand/	8.9 percent
	bound with H/	91.0 percent
PO_4		
	bound with Ca/	3.4 percent
	bound with Mg/	2.9 percent
	bound with Mn/	.1 percent
	bound with Cu/	.2 percent
	bound with H/	93.3 percent
Ac		
	as a free ligand/	99.8 percent
	bound with Ca/	.1 percent
Cit		
	bound with Al/	100.0 percent
Ox		
	as a free ligand/	77.1 percent
	bound with Ca/	20.1 percent
	bound with Mg/	2.3 percent
	bound with Cu/	.1 percent
	bound with Zn/	.2 percent
Sal		
	bound with H/	99.9 percent
Tart		
	as a free ligand/	96.4 percent
	bound with Ca/	3.0 percent
	bound with Mg/	.5 percent
Gly		
	as a free ligand/	1.3 percent
	bound with Mg/	.4 percent
	bound with Cu/	6.5 percent
	bound with H/	91.7 percent
Glut		
	as a free ligand/	1.2 percent
	bound with Cu/	6.7 percent
	bound with Zn/	.5 percent
	bound with H/	91.5 percent
Cyst		
	bound with Zn/	62.7 percent
	bound with Pb/	23.1 percent
	bound with H/	14.1 percent

Orn	
bound with Ca/	.3 percent
bound with Mg/	.2 percent
bound with Cu/	9.5 percent
bound with H/	89.9 percent
Lys	
bound with H/	99.9 percent
Asp	
as a free ligand/	1.9 percent
bound with Cu/	14.3 percent
bound with Zn/	.7 percent
bound with Ni/	.4 percent
bound with H/	82.7 percent
Ser	
as a free ligand/	6.6 percent
bound with Cu/	2.1 percent
bound with H/	91.2 percent
Ala	
as a free ligand/	1.3 percent
bound with Cu/	6.5 percent
bound with Zn/	.1 percent
bound with H/	92.0 percent
Tyr	
as a free ligand/	3.2 percent
bound with Mg/	.1 percent
bound with H/	96.5 percent
Met	
as a free ligand/	6.7 percent
bound with H/	93.1 percent
Phe	
as a free ligand/	5.0 percent
bound with Cu/	8.0 percent
bound with H/	87.0 percent
Leu	
as a free ligand/	2.0 percent
bound with Cu/	9.1 percent
bound with H/	88.8 percent
Pro	
as a free ligand/	.2 percent
bound with H/	99.8 percent

HVO_4	
as a free ligand/	45.4 percent
bound with H/	54.6 percent
Mal	
as a free ligand/	97.3 percent
bound with Ca/	1.2 percent
bound with H/	1.5 percent
For	
as a free ligand/	99.7 percent
bound with Ca/	.2 percent